

SPECTRAL AND PHOTOPHYSICAL PROPERTIES OF 1-PYRAZINYL-2-(3-QUINOLINYL)ETHYLENE

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Abstract—The spectral and photophysical properties of *trans*-1-pyrazinyl-2-(3-quinolinyl)ethylene (*trans*-3-PyQE) are investigated under various conditions in order to obtain information on ground and excited states. The absorption spectrum of *trans*-3-PyQE changes slightly with varying degree of solvent polarity; the fluorescence spectrum is shifted to the red and becomes broad and structureless as the solvent polarity increases. The fluorescence quantum yield increases with increasing solvent polarity. The fluorescence intensity of *trans*-3-PyQE decreases as the concentration of methyl iodide increases. The fluorescence spectra of *trans*-3-PyQE changes markedly upon the variation of the excitation wavelength, presumably due to an equilibrium between conformers originating from the rotation of a quasi-single bond between the quinolinyl group and ethylenic carbon atom. These results indicate that the spectral and photophysical properties of *trans*-3-PyQE are strongly influenced by solvent, heavy atom, and an equilibrium between conformers

INTRODUCTION

The photochemical and photophysical properties of aza and diaza analogues of stilbene have received a lot of interest for a long time.^{1,2} Because of the proximity of the $^1(\pi, \pi^*)$ state to the $^1(n, \pi^*)$ state introduced by the heteroatom, the photochemical and photophysical properties of the compounds are markedly different from those of the corresponding hydrocarbons.¹ It has also been proposed that the vibronic perturbation (the proximity effect) of the lowest close-lying $^1(\pi, \pi)$ and $^1(n, \pi^*)$ for many nitrogen containing heterocyclic compounds leads to an efficient internal conversion or intersystem crossing. Because of the proximity of these states, intersystem crossing is tremendously enhanced in pyrazine ($\Phi_{\text{fl}} \approx 0$, $\Phi_{\text{isc}} \approx 1.0$, $\Phi_{\text{ph}} \approx 1.0$) compared to benzene ($\Phi_{\text{isc}} \approx 0.25$, $\Phi_{\text{fl}} \approx 0.05$) and pyridine ($\Phi_{\text{ic}} \approx 1.0$).²

It has been already demonstrated that the direct photoisomerization of 1,2-bis-pyrazinylethylene (BPyE)³ and 1-pyrazinyl-2-(4-quinolinyl)ethylene (4-PyQE)⁴ proceeds through a triplet manifold in contrast to stilbene.⁵ Previously, it was also reported that the fluorescence and excitation spectra of *trans*-2-styrylquinoxaline (2-StQx) changed markedly on the variation of the excitation and emission wavelengths, due to an equilibrium between conformers originating from the rotation of a quasi-single bond between the quinoxalyl group and the ethylenic carbon atom.⁶

Trans-1-Pyrazinyl-2-(3-quinolinyl)ethylene (3-PyQE), which is a triaza analogue of 2-styrylnaphthalene (2-StN), has both photophysical and steric abnormalities with respect

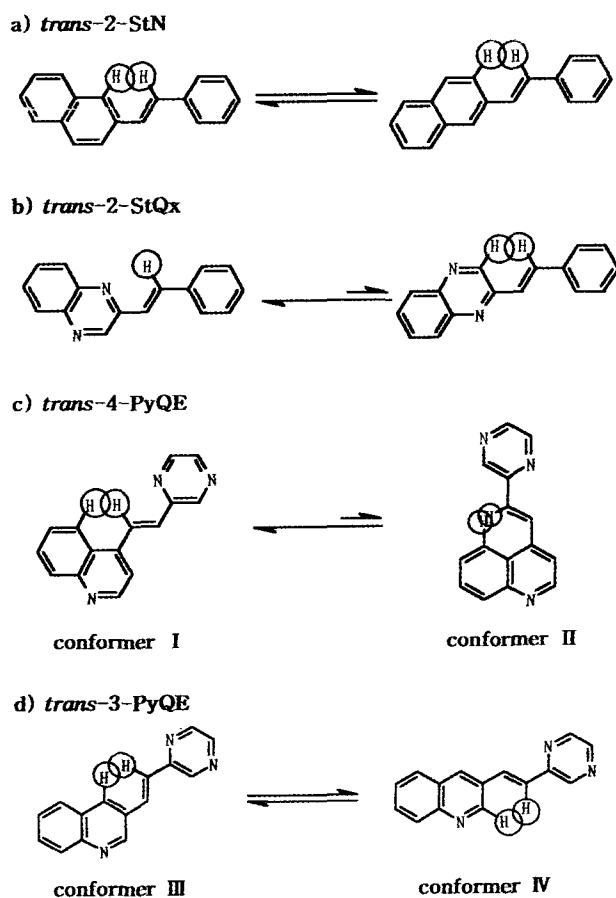
to 2-StN⁷ and in contrast to 4-PyQE.⁸ The replacement of the naphthyl and phenyl groups of 2-StN by quinoline ($\Phi_{\text{fl}} < 10^{-4}$)⁹ and pyrazine rings makes the lowest $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states very close to each other. *Trans*-3-PyQE, therefore, is an attractive candidate for spectroscopic and photochemical studies due to the proximity of the close-lying lowest $^1(n, \pi^*)$ and $^1(\pi, \pi^*)$ states. Moreover, an increase in planarity as the result of lower steric crowding,⁷ which originates from nitrogen heteroatoms in the ortho position of the pyrazinyl group, should result in the change of the conformational equilibrium and photophysical parameters of *trans*-3-PyQE conformers with respect to those of *trans*-2-StN and *trans*-2-StQx⁶ (Scheme 1).

In this study, therefore, spectral and photophysical properties of *trans*-3-PyQE were investigated under various conditions to elucidate the role of nitrogen heteroatoms in the conformational equilibrium. Results are compared with those for aza, diaza and triaza analogues of stilbene and styrylnaphthalenes (StN's) such as *trans*-naphthyl-pyridylethylenes (NPE'S), *trans*-2-StQx and *trans*-4-PyQE.

MATERIALS AND METHODS

Materials. Extra pure solvents were used as received or after distillation by standard methods prior to use. *Trans*-3-PyQE was prepared by the condensation of 3-methylquinoline with pyrazinecarbaldehyde in acetic anhydride at ca. 170°C like as *trans*-4-PyQE^{4,8} and was recrystallized twice from n-hexane. *Cis*-3-PyQE was prepared from *trans* isomer by photoisomerization and was isolated by low pressure preparative liquid chromatography (column, Lichro-prep RP-8 Lobar prepacked col-

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Scheme 1. Conformational Equilibrium

umn ; detector, Bio-Rad Model 1300 UV monitor at 280 nm ; eluting solvents, water/methanol/ tetrahydrofuran (35:45:6, v/v). The purity of the *trans* and *cis* isomers was proven by high performance liquid chromatography on a Waters Association Model 244 HPLC equipped with a Model 6000A solvent delivery system and a Model 440 absorbance detector at 280 nm (column, μ -Bondapak C18 (3.9 mm ID \times 30 cm) column ; eluting solvents, water/methanol/tetrahydrofuran (28:40:6, v/v).

Trans-3-PyQE : $^1\text{H-NMR}$ (CDCl_3) δ 9.28 (d, 1H, $J=2\text{Hz}$, quinolinic 2'-H), 7.6~8.9 (m, 9H, aromatic and PyCH=), 7.53 (d, 1H, $J=16\text{Hz}$, QCH=, *trans*) ppm ; $^{13}\text{C-NMR}$ (CDCl_3) shows 13 peaks, δ 150.5, 149.2, 144.3, 143.8, 143.1, 133.5, 131.6, 129.6, 129.3, 129.0, 127.9, 127.0 and 125.9 ppm ; MS m/z (EI) 233(M^+ , 85), 232(M^+-H , 100), 205(M^+-HCN , 15), 179($\text{M}^+-\text{H}_2\text{C}_2\text{N}_2$, 19).

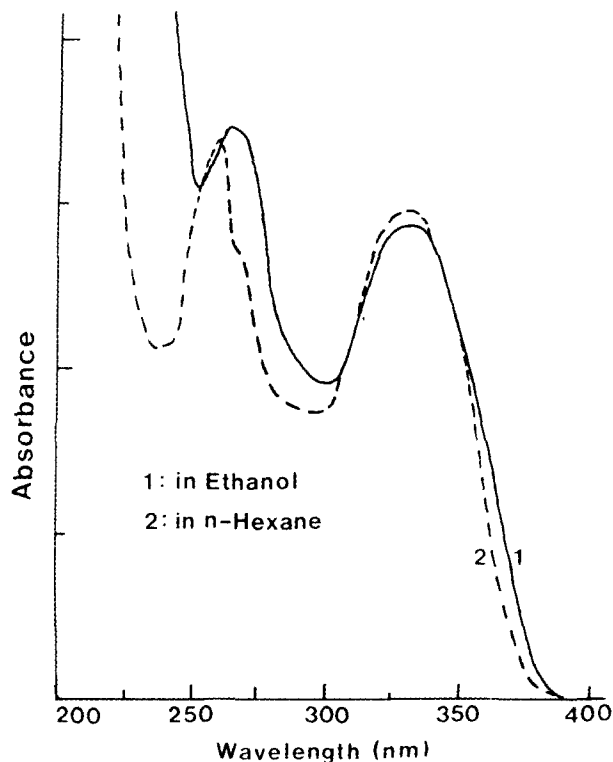
Spectra and Quantum Yield Measurements. The apparatus and techniques for quantum yield measurement have been described previously.⁸ UV absorption spectra were recorded on a Cary 17 spectrophotometer or a Hitachi 330 spectrophotometer. Fluorescence spectra were measured on an Aminco-Bowman spectrofluorometer or JASCO FP 770 spectrofluorometer. For the corrected spectra, rhodamine B was used as a quantum counter. The fluorescence quantum yields at room temperature were determined by three of four independent experiments using quinine sulfate ($\Phi_{\text{fl}}(298\text{K}) = 0.55$ in 1.0 N H_2SO_4)

and/or 9,10-diphenylanthracene ($\Phi_{\text{fl}}(298\text{K}) = 1.0$ in cyclohexane) as standards.¹⁰ Quantum yields obtained with respect to the two standards were in good agreement with each other (standard deviation, about 5%). The maximal optical density of the solution used for determination of the fluorescence quantum yields were less than 0.1 in a cell 1 cm thick and all quantum yields were corrected for the difference between the refractive indices of solvents.

RESULTS AND DISCUSSION

Spectral properties

The absorption spectra of *trans*-3-PyQE shown in Figure 1 are somewhat different from those of the corresponding hydrocarbons, being similar to those of other aza analogues such as *trans*-4-PyQE⁸ and *trans*-2-StQx.⁶ The absorption bands at about 330 nm and 250 nm are probably due to the ethylenic (π, π^*) transition and quinolinic band, respectively. It is noteworthy that the long wavelength ethylenic band is slightly red-shifted with respect to the bands of the corresponding hydrocarbons and other aza analogues (315 nm for both *trans*-2-StN¹¹ and *trans*-3-StQ¹²). As reported earlier for aza analogues with nitrogen heteroatoms in the ortho position,^{8,13} the shift reflects the increase in the conjugation of the *trans*-3-PyQE conformers with the increased planar structure, which is a result of lower steric crowding than *trans*-

Figure 1. UV absorption spectra of *trans*-3-PyQE.

2-StN and *trans*-2-StQx as shown in scheme 1.

The (n, π^*) band does not appear in the absorption spectra and seems to be submerged in the more intense (π, π^*) band. However, the absorption at long wavelength (> 370 nm), which can be attributed to the (n, π^*) transition, is red-shifted when the solvent polarity is increased with respect to *trans*-4-PyQE.⁸ This phenomenon can not be ascribed to the effect of solvent polarity because the spectrum induced by the (n, π^*) transition should be red-shifted as the solvent polarity decreases, due to the decrease in the energy level of the $^1(n, \pi^*)$ state and the increase in the energy level of the $^1(\pi, \pi^*)$ state. As shown in scheme 1, for *trans*-4-PyQE, since conformer II has larger steric hindrance between the quinolinic hydrogen and ethylenic hydrogen, conformer I may dominate in equilibrium. For *trans*-3-PyQE, however, conformer III and IV may exist at near equimolar fractions due to the similar stabilities. The shift of absorption spectrum toward the longer wavelength for *trans*-3-PyQE, therefore, probably manifest the equilibrium between two conformers (III and I), not the polarity effect of solvent.

Similar to the emission spectra of many naphthyl analogues of 1,2-diarylethylene,^{7,11,14} the fluorescence spectrum of *trans*-3-PyQE is slightly structured in n-hexane at room temperature, as shown in Figure 2. However, the spectra become broader and structureless, and the maxima are red-shifted as the polarity of solvent increases (Table 2 and Figure 2). The fluorescence quantum yield of *trans*-3-PyQE is much smaller than that of stilbene, *trans*-4-PyQE,⁸ and *trans*-2-StQx.⁶ These results strongly suggest that the efficient radiationless

transition (internal conversion or intersystem crossing), due to the extensive vibronic mixing (proximity effect) between close-lying $^1(\pi, \pi^*)$ and $^1(n, \pi^*)$ states, is the major deactivation processes of *trans*-3-PyQE, as was observed for other aza analogues.¹ The fluorescence quantum yield of *trans*-3-PyQE in an inert solvent at room temperature also lies between those of ortho (2-styrylpyridine (2-StP), $\Phi_f = 0.0008$ and 2,2'-dipyridylethylene (2,2'-DPE), $\Phi_f = 0.005$) and meta (3-styrylpyridine (3-StP), $\Phi_f = 0.075$ and 3,3'-dipyridylethylene (3,3'-DPE), $\Phi_f = 0.13$) azastilbenes,¹⁵ similarly to *trans*-BPyE.³ This can be ascribed to the lower thermal barrier exerted by π and π^* orbitals which have nodes in the meta position of the nitrogen atoms, the corresponding to ortho and meta positions in 3-PyQE as in 2-StP and 2,2'-DPE, and 3-StP and 3,3'-DPE.

Furthermore, on changing the excitation wavelength, the fluorescence quantum yield in ethanol changes from 0.016 at $\lambda_{ex}=290$ nm to 0.007 at $\lambda_{ex}=360$ nm and a large difference between the fluorescence maxima is also observed as shown in Table 1. When *trans*-3-PyQE was excited at $\lambda_{ex}=330$ nm (wavelength at absorption maxima) and 370 nm (the edge of the absorption spectrum), both of the fluorescence quantum yield and the maxima become different, while the fluorescence (broad) remains unchanged. This behavior is probably related to the equilibrium between the two conformers of *trans*-3-PyQE, similarly to *trans*-2-StQx.⁶ The absorption and fluorescence spectra of *trans*-3-PyQE described above are probably the sum of those for each conformer in equilibrium (*i.e.* equilibrium between two conformers of different planarity and polarity, the more polar and planar conformer being predominant in solution)

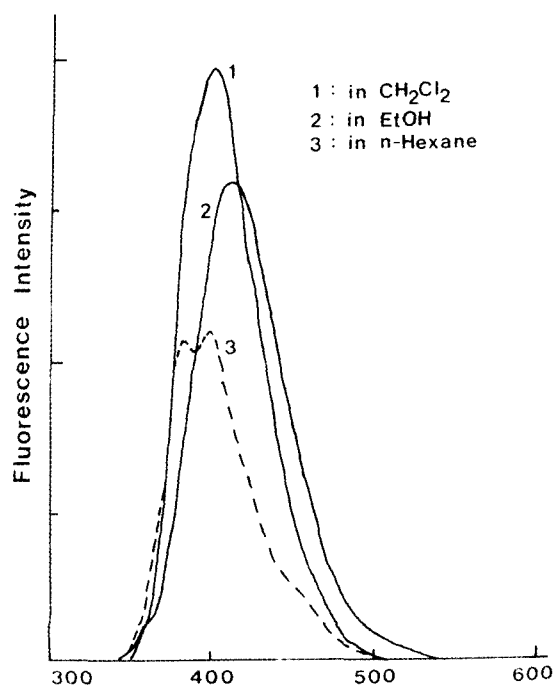


Figure 2. Fluorescence spectra of *trans*-3-PyQE.

Heavy atom effect on fluorescence

As observed in *trans*-BPyE¹⁶ and *trans*-4-PyQE,⁸ the fluorescence intensity of *trans*-3-PyQE decreases as the concentration of methyl iodide increases, probably due to an

Table 1. Fluorescence quantum yields Φ_f and fluorescence maxima λ_{fl}^{max} of *trans*-3-PyQE in ethanol at different excitation wavelengths λ_{ex} .

| λ_{ex} (nm) | λ_{fl}^{max} (nm) | Φ_f |
|---------------------|---------------------------|----------|
| 290 | 412 | 0.016 |
| 300 | 412 | 0.016 |
| 310 | 410 | 0.016 |
| 320 | 410 | 0.016 |
| 330 | 409 | 0.016 |
| 340 | 409 | 0.011 |
| 350 | 403 | 0.009 |
| 360 | 412 | 0.007 |
| 365 | 416 | 0.008 |
| 370 | 422 | 0.010 |

increase in intersystem crossing when the heavy atom is added. Data for the fluorescence quenching of *trans*-3-PyQE by MeI exhibit a good linear Stern-Volmer relationship (Figure 3) with a slope of 19.8 M^{-1} in methanol-water (1:1, v/v) solution. Assuming the quenching rate to be the same as the diffusion-controlled rate ($k_q = k_{\text{diff}} = 9.8 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$), the calculated fluorescence lifetime is 2.02 nsec in methanol-water (1:1, v/v) solution. This value is larger than those of stilbene, azastilbenes, diazastilbenes, and BPyE,^{1,3,15} lying between that of β ,2-naphthylpyridylethylene (β ,2-NPE) which is an ortho aza analogue and β ,3-NPE which is a meta aza analogue of styrylnaphthalenes.¹⁷ This is probably due to the presence of a quinoline (in the meta position of nitrogen atom) and a pyrazine (in the ortho and meta positions of nitrogen atoms) rings and the lowest $^1(\pi, \pi^*)$ state similar to the fluorescence quantum yield as previously described.

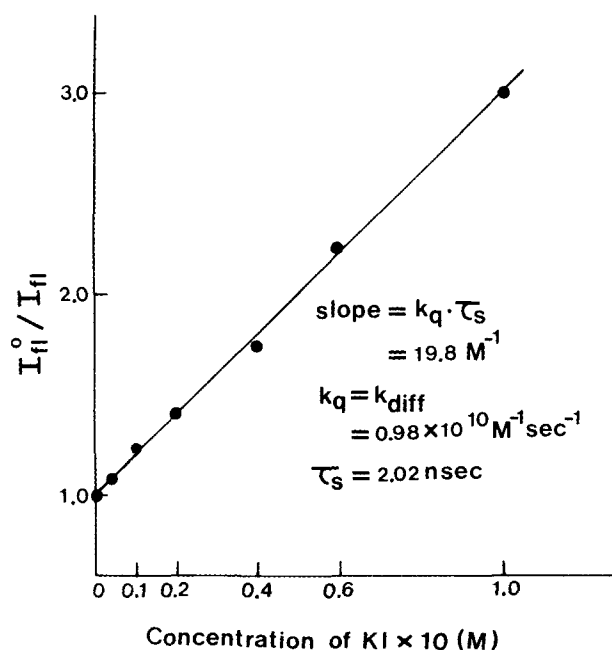


Figure 3. Stern-Volmer plot of the fluorescence quenching of *trans*-3-PyQE by KI in methanol/water (1:1, v/v)

Solvent effects on the fluorescence quantum yields

Values of the fluorescence quantum yields and the maxima of the fluorescence spectra ($\lambda_{\text{fl}}^{\text{max}}$) of *trans*-3-PyQE in various solvents (320 nm excitation) are summarized in Table 2. The quantum yields increase as the polarity of the solvent increases, which is probably due to the change in the electronic configuration of the lowest excited singlet state from $^1(n, \pi^*)$ to $^1(\pi, \pi^*)$ upon the increase of the solvent polarity. Aloisi *et al.*¹⁸ have already reported that the fluorescence quantum yields of styrylnaphthalenes (StN's), which has no $^1(n, \pi^*)$ state, decrease markedly as the polarity of the solvent increases. As mentioned previously, however, the flu-

orescence quantum yield of *trans*-3-PyQE is affected by the excitation wavelength, and the fluorescence spectra is the sum of those for each conformers in equilibrium. If two conformers are in equilibrium at ground state and not at excited state, one conformer in excited state being fluorescent but the other is not fluorescent, the fluorescence quantum yields and the maxima in various solvents are consistent with the variation of excitation wavelengths mentioned above.

Table 2. Fluorescence quantum yields ϕ_{fl} and fluorescence maxima $\lambda_{\text{fl}}^{\text{max}}$ of *trans*-3-PyQE in various solvents at 320 nm excitation.

| Solvents | $\lambda_{\text{fl}}^{\text{max}}$ (nm) | ϕ_{fl} |
|----------------------------------|---|--------------------|
| n-Hexane | 390 | 0.007 |
| Diethyl ether | 403 | 0.005 |
| Tetrahydrofuran | 403 | 0.006 |
| Dichloromethane | 403 | 0.015 |
| Ethanol | 410 | 0.016 |
| Methanol | 418 | 0.016 |
| MeOH/H ₂ O (9:1, v/v) | 419 | 0.017 |
| MeOH/H ₂ O (7:3, v/v) | 421 | 0.023 |
| MeOH/H ₂ O (5:5, v/v) | 423 | 0.025 |
| MeOH/H ₂ O (3:7, v/v) | 428 | 0.025 |
| MeOH/H ₂ O (1:9, v/v) | 434 | 0.025 |

Gennaro *et al.*^{12,19} also reported that the potential energy surfaces of the two electronically excited conformers of 3-StQ have rather different properties, so that one of the excited conformers is deactivated mainly through the fluorescence emission, and the other through a photochemical channel like the *trans* \rightarrow *cis* geometrical isomerization. In addition, the conformers of the naphthyl derivatives (*trans*-2-StN and *trans*-2,2-dinaphthyl-ethylene (2,2-DNE))^{7,20} and their aza analogues (*trans*-3-StQ and *trans*-naphthylpyridyl-ethylenes (NPE's))^{12,21} show multiple fluorescence which is dependent on both the excitation and the emission wavelengths.

From these results, it can be concluded that the large solvent dependence of the fluorescence is probably due to the change in the electronic configuration of the lowest excited singlet state and also due to the difference in solvent dependences of the photophysical parameters of two conformers, although a change in the position of the conformational equilibrium depending on the solvents can not be excluded completely.

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